Studies on Fluorine at Low Temperatures. VIII. Determination of Molecular Heat, Heat of Fusion of Condensed Fluorine and the Entropy of Fluorine.

By Eizo KANDA.

(Received August 12th, 1937.)

The molecular heats of oxygen, nitrogen and other ordinary elements in the forms of condensed gases have been determined at low temperatures, and accordingly their entropies are already known. But such determinations have not been made at all on fluorine and volatile fluorides (except hydrogen fluoride). The present author measured the specific heat of fluorine at low temperatures, and in addition, determined the melting point, heat of fusion and entropy of fluorine, using a method by which he previously measured the specific heat of organic compounds at low temperatures.[1]

I. Method and Apparatus. The apparatus for the experiment is shown in Fig. 1.

(1) *Cooling device.* The measurement was made in a range from −190°C. to −258°C., the cooling being done by liquid nitrogen or liquid hydrogen or solid hydrogen. The apparatus illustrated in Fig. 1 is for cooling by solid hydrogen or liquid hydrogen. In this apparatus, A is a Dewar vessel made of German silver which is intended for liquid nitrogen, and B is a glass Dewar vessel for liquid hydrogen. B has a brass cap D in its upper part, which is connected with the Dewar vessel by means of rubber packing and is kept air-tight. The cap D has an opening at which the calorimeter is held, an opening for the double-walled pipe through which liquid hydrogen is poured in, a device for indicating the depth of liquid hydrogen, an opening at which the mercury pressure gauge is held, and an exhaust opening. Filling B with liquid hydrogen is done by connecting it with V_1 by means of the double-walled pipe, and the liquid is sucked in by a pump attached to M.

For lowering the temperature of the liquid hydrogen under its boiling point −252°C., the pump of large capacity attached to M is worked, and the liquid is vaporized vigorously at the decreased pressure. When

(1) Aoyama and Kanda, *Sci. Repts. Tôhoku Imp. Univ.*, Ser. I, **24** (1935), 116.

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the vapour pressure of the liquid hydrogen is 40 mm., the hydrogen gradually solidifies, and reaches the triple point, that is, −258°C.

(2) *Apparatus for determining the temperature.* Inside the device for measuring the specific heat, there is a platinum resistance thermometer which is made by winding a platinum thread around a copper cylinder insulated with bakelite. The precision of this thermometer is determined in advance by comparing its resistance with the temperature of the gas thermometer.[2] The resistance is shown in Table 1.

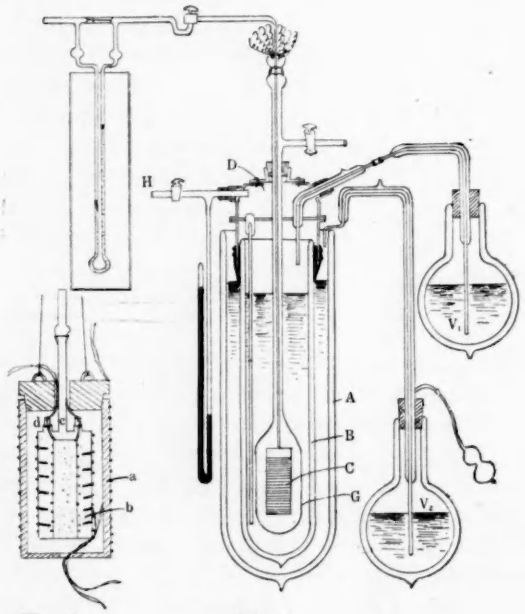


Fig. 2.

Fig. 1.

Table 1.

Temperature (°C.)	Resistance (ohm)
0°	20.1550
−25.50	18.2597
−39.10	17.1710
−68.38	14.8130
−125.55	10.1146
−158.75	7.3203
−183.40	5.2059
−195.85	4.2633
−252.66	0.9652
−254.53	0.8154
−256.50	0.6637
−258.17	0.5324

At temperatures lower than −252.66°C., the calibration was made by means of a hydrogen vapour thermometer.[3]

According to the formula

(2) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

(3) Wrede-Rankine-Keesom's formula (Onnes and Keesom, *Commun. Phys. Lab. Univ. Leiden*, Suppl. No. 23) is used, which is

$$\log p_{\text{cm.}} = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2}.$$

$$R_t = aR_0\left[\frac{1}{a}+t+\delta\left(1-\frac{t}{100}\right)\frac{t}{100}+\beta\left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right],$$

the relation between the resistance and the temperature at −252.66°C. and upward can be expressed in

$$R_t = 0.0038745 \times 20.1550 \times \left[258.097+t+1.4950 \times \left(1-\frac{t}{100}\right)\frac{t}{100}+ 0.11251 \times \left(1-\frac{t}{100}\right)\left(\frac{t}{100}\right)^3\right].$$

(3) *Apparatus for measuring the specific heat.* The apparatus for measuring the specific heat was nearly the same as one formerly used in the measurement on organic substances, but was made suitable for condensed gases.

In Fig. 2, a is a case made of a thick copper plate. The temperature is adjusted by means of a heating coil around the outside of the case. b is a cylinder made of a thin copper plate and has a resistance thermometer and a few ledges in it with a heating coil of a constantan wire on the outside. There are junction points of a thermocouple on the inside and outside of a and b respectively for determining the difference in temperature between the two sides. The exit d for the platinum resistance wire is sealed with fused glass as shown in the figure. The sample is introduced through C and condensed in b. This device is put in a glass bulb G, which is set up in the cooling vessel.

(4) *Determination of the amount of the sample.* The determination of the amount is very difficult in the case of condensed gases. This is especially the case with fluorine, for which a gas reservoir cannot be used. The author used a 200 c.c. gas-burette, in which glycerine was placed on the mercury as shown in Fig. 3.

(5) *Apparatus for determining the heating energy.* The electrical connections for measuring the temperature of the sample and heating energy electrically applied to the calorimeter are illustrated in Fig. 4. To make the construction of the device well understood and to give an exact idea of the apparatus, the platinum thermometer, the sample, the heating coil, and the case are separately illustrated.

The measuring apparatus consists of a system in which the current in the heating coil and the potential difference between the ends of the coil are measured and of a system in which the resistance of the platinum thermometer is measured. In both systems there are standard resistances connected with the potentiometers. The heating energy was

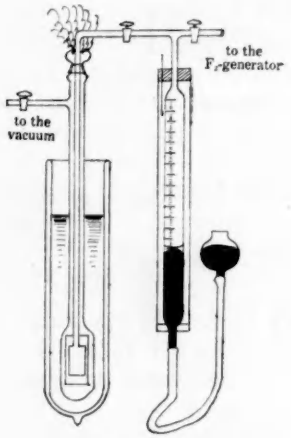


Fig. 3.

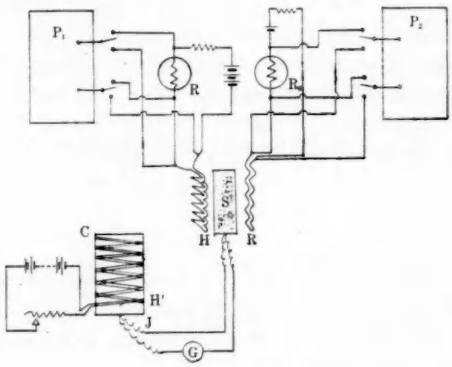


Fig. 4.

determined by means of the Leeds and Northrup type potentiometer, and the potentiometer for low potential free from thermoelectromotive force was used for the resistance thermometer.

(6) *Construction of the calorimeter and heat loss.* For obtaining a desired low temperature, dry air or dry hydrogen gas was introduced into the glass bulb G in Fig. 2, and the low temperature of the liquid nitrogen or liquid hydrogen on the outside was transmitted to the case and the calorimeter by conduction of this gas. The temperature of the sample was observed by means of the platinum thermometer, and when a proper temperature was reached, G was cleared of the hydrogen gas, and was made highly vacuous (about 10^{-5} mm. Hg). In this way the inward transmission of cold through the wall of G was prevented. Further, for preventing cooling of the calorimeter by conduction of any remaining gas, the case was heated slowly through the coil on its surface. The difference in temperature between the outer surface of the colorimeter and the inner surface of the case was observed even while the specific heat was being measured by means of a galvanometer, and the heating current on the case was adjusted during the rise of temperature so that the difference might not exceed 0.5°. Although this process is far more complicated than one in which the calorimeter is simply hung in G, it greatly decreases the heat loss due to radiation and conduction, and minimizes the error.

Supposing that the vacuum in G is about 10^{-5} mm. Hg, that the temperature at which the specific heat is to be measured is −200°C., and that

the difference in temperature between the walls of G and b is 50°, the heat loss of the calorimeter due to radiation q_r and due to conduction q_g will be approximately expressed by

$$q_r \fallingdotseq \frac{F_i}{\frac{1}{C}+\frac{F_i}{F_e}\left(\frac{1}{C}-\frac{1}{C_b}\right)}(T_e^4-T_i^4) \fallingdotseq F_iC(T_e^4-T_i^4)\ , \quad \text{and}$$

$$q_g = \frac{a}{2-a}\eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i \fallingdotseq \eta p\sqrt{\frac{273}{T_i}}(T_e-T_i)F_i\ ,$$

where F_i is the surface area of the calorimeter, F_e that of glass bulb G, T_i temperature of the calorimeter, T_e the surface temperature of G, C radiation constant of the material of the calorimeter, etc., C_b that of the black body, a the accommodation coefficient of the gas (air or hydrogen), η a constant dependent upon the viscosity, and p the pressure of the remaining gas (mm. Hg).

For example, in case F_i=50 cm.^{2}, T_i=73°K (−200°C.), and T_e=23°K (−250°C.), we have $q_r=5.86\times10^{-5}$ cal./sec., and $q_g=27.8\times10^{-5}$ cal./sec.

In the actual measurement, the temperature of the sample is raised usually by 0.2° for every 5 minutes. For 5 minutes $q_r'=0.0176$ cal., $q_g'=0.0834$ cal., and $\Sigma q'=0.101$ cal.

The test fluorine (about 20 g.) actually requires about 1 cal. at this temperature or neighbourhood for a rise of 0.2°, and so the above-mentioned heat loss amounts to more than 10%. If, however, the temperature of the wall of the case is kept at −199.5°C. by adjusting against −200°C. of the device, we shall have $\Sigma q'=0.0088$ (for 5 minutes).

This shows that the heat loss is about 0.9% of the heat required. In this way the heat loss must be kept small for making the experiment with a very small temperature rise of the sample and for obtaining a specific heat as near the true one as possible.

II. Measurment of Specific Heat. (1) Quantity of heat which is electrically given is (a) consumed in the temperature rise of the sample and (b) consumed in the temperature rise of the calorimeter itself, and (c) escapes outward, resulting in heat loss.

$$Q = I^2RZ = (CM+w)\times\Delta t+q = (CM+w)\times\Delta t'\ ,$$

where I is electric current flowing through the heating coil of the calorimeter, R resistance of the heating coil of the calorimeter, Z duration of heating, C specific heat of the sample, M mass of the sample, w water

equivalent of the device, and Δt rise of the temperature. Of these, w was determined in advance at various temperatures.

The heat escaping outward was, as stated before, about 1 to 2%, and was determined experimentally by a temperature-time curve. Thus the specific heat of the sample could be determined by the foregoing formula.

(2) *Correction for the heat loss and determination of the temperature rise.* As for the correction for the heat loss and the determination of the true temperature rise, the resistance of the platinum thermometer and the time were observed before and after the heating of the sample and the temperature-time curve was constructed (Fig. 5). From this curve the true rise of temperature was obtained. For instance, let us suppose that the temperature of the sample is not kept perfectly constant but has a tendency slightly to rise before the heating (A–B) and that the heating is begun at B (the time Z_1) and ends at C (the time Z_2), the sample then gradually being cooled along the C–D line. The lines AB and CD are extended as in the figure, and F is taken on the extension of the DC line so that ΔZ may be equal to BCE/Δt. If G is the point of intersection of the ordinate through F and the extension of the AB line, FG=$\Delta t'$ will be the true rise of temperature. The area BCE is determined on section paper.

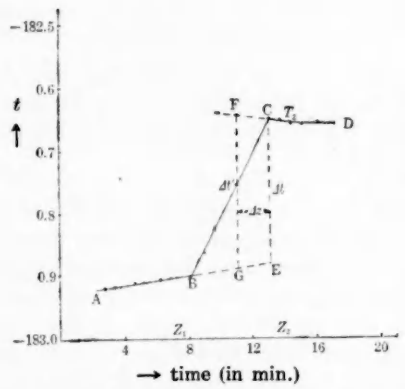


Fig. 5.

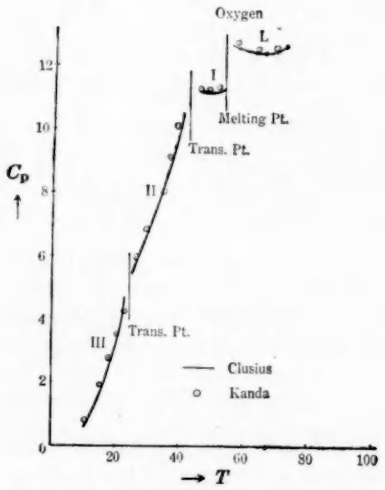


Fig. 6.

(3) *Water equivalent of the calorimeter.* See Table 2.

Table 2.

Temperature	Water equivalent	Temperature	Water equivalent
0°	2.141	−159.17	1.608
−15.50	2.120	−172.15	1.521
−37.85	2.074	−185.55	1.480
−50.17	2.041	−192.50	1.293
−58.56	2.024	−199.13	1.209
−67.21	2.005	−207.21	1.121
−86.17	1.950	−211.50	1.063
−94.54	1.921	−219.10	0.941
−103.13	1.889	−225.86	0.841
−118.55	1.821	−232.10	0.705
−127.34	1.782	−238.11	0.558
−134.85	1.744	−250.18	0.221
−145.76	1.690	−258.22	0.0045

III. Results of the Measurements. (1) *Oxygen.* In the preliminary experiment, measurement was carried out on liquid oxygen and solid oxygen. It was intended only for comparing its result with those already obtained by Eucken[4] and Clusius[5] (see Fig. 6). The values are shown in Table 3. The values obtained in the author's experiment were somewhat greater than those obtained by Clusius for liquid and solid I, but were close to the values reached by Eucken, which, however, are not given here.

Table 3.

Author	Eucken	Clusius	Kanda
Transition point I	23.5°K	23.8°K	24.1°K
„ „ II	42.5	43.5	42.9
Melting point	54.1	54.1	54.3

(2) *Fluorine.* The quantity of the sample used in each experiment was about 0.5 mol. The result as reduced to the molecular heat according to the value of specific heat is tabulated below.

(4) Eucken, *Verhandl. Phys. Ges.*, **18** (1915), 4.
(5) Clusius, *Z. physik. Chem.*, B, **3** (1929), 41.

(a) Molecular heat. See Table 4.

Table 4.

T	C_p	C_v	θ	T	C_p
14.91	1.167	11.59	99.8	47.95	7.741
17.75	1.807	1.786	100.2	52.98	8.210
20.01	2.240	2.203	101.0	53.98	8.761
23.10	2.841			55.20	Melting point
25.42	3.440			57.50	10.84
29.50	4.310			62.51	10.92
32.00	4.795			67.49	10.98
35.40	5.561			77.10	11.12
39.11	6.280			83.41	11.20
43.10	7.120			85.19	Boiling point

(b) Melting point and heat of fusion. According to thermal analysis, the melting point is 55.20°K. The heat of fusion was determined by measuring the total heat quantity used for heating from a point a little below the melting point up to a point a little higher than this point, and by subtracting from this total heat quantity the sensitive heat used for the respective rises of temperature from the values of the specific heat of the solid and liquid. The heat of fusion is Q_s=372 cal./mol. The value of C_p is given in Fig. 7.

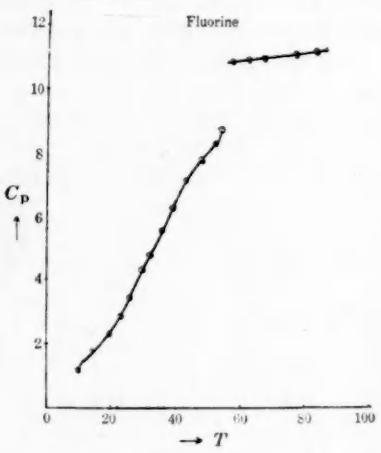


Fig. 7.

IV. Characteristic Temperature and Entropy as Determined from the Result of Measurements. (1) *Characteristic temperature.* Debye's law of T^3 for the atomic heat at constant volume is, strictly speaking, applicable only in the case of a monatomic and cubic system. But if the molecule of crystal of solid fluorine also can be regarded as making Debye's vibration at a temperature below 20°K as if it were a single atom, its molecular heat may be said to be proportional to the cube of

the absolute temperature. On this assumption, the characteristic temperature Θ was obtained from the molecular heat at three points below 20°K.

For determining the molecular heat at constant pressure, the following formula was used:

$$C_v = C_p - 0.0214 \frac{T}{T_s} C_p^2 ,$$

where T_s is the melting point, 55.20°K.

The characteristic temperature Θ was determined from the value of C_v by using

$$C_v = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta}\right)^3 .$$

The results obtained at three points below 20°K well coincide with one another and show the above-mentioned assumption is right. Thus we have $\Theta = 100.3$.

(2) *Entropy of fluorine vapour.* The entropy of fluorine vapour is obtained from

$$S = \int_0^T \frac{C_p}{T} dT .$$

There being no measured value of the molecular heat at temperatures below 15°K, the author made integration, using Debye's function and putting $\Theta = 100.3$.

For determining $\int_0^T \frac{C_p}{T} dT$ as to the solid and liquid between 15°K and 55.2°K, and 56.2°K and 85.19°K, by using $T_s = 55.2$, $Q_s = 372$ cal. at the melting point and $T_o = 85.19$, $Q_o = 1581$ cal. (from the vapour pressure data) at the boiling point, a curve is drawn for the measured values of C_p at various temperatures against $\ln T$, and mensuration was graphically made of $\int C_p d \ln T$.

Further, to the value of entropy of such an ideal gas must be added correction for the entropy of a real gas.

From Berthelot's equation of state

$$PV = RT\left[1 + \frac{9}{128} \frac{PT_c}{P_c T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right],$$

where T_c is the critical temperature (144 for fluorine) and P_c is the critical pressure (55 atm.), and from the thermodynamical relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we have

$$\Delta S = S_{\text{real}} - S_{\text{ideal}} = \frac{27}{32} R \frac{T_c^3}{T^3} \frac{P}{P_c}.$$

Putting $T=85.19°K$ (boiling point), $T_c=144°K$, $P_c=55$ atm., and $P=1$ atm. in this equation, we have $\Delta S=0.15$ cal./degree mol.

In fine, the entropy of fluorine vapour at the boiling point of 85.19°K is as follows:

$\int_0^{15} \frac{C_p}{T} dT = 0.49$ according to Debye's law, $\int_{15}^{55.2} C_p d \ln T = 5.86$ from the molecular heat of solid, $Q_s/T_s = 6.73$ at melting point, $\int_{55.2}^{85.19} C_p d \ln T = 5.46$ from the molecular heat of liquid, $Q_v/T_v = 18.60$ at boiling point, $\Delta S = 0.15$ correction for real gas, entropy of fluorine vapour at boiling point = 37.29 entropy unit.

Conclusion. As the results of the investigations recorded in the papers I–VIII the various properties of fluorine, knowledge of which is necessary for the study of fluorine at low temperatures, have been made clear. The experiments, however, were of such a nature that one or two instruments or apparatus were not enough for dealing with several kinds of materials or problems, but one material had to be studied from various points of view, and therefore various apparatus had to be devised for the purposes. Of these apparatus, some will not stand further use, because their lives have been exhausted by the highly corrosive nature of fluorine, while others will be usable in future studies of condensed gases.

In conclusion the author expresses his deepest gratitude to Prof. Aoyama, who advised him to get about the present investigation and who kindly directed him throughout his work. And he also wishes to express his heartful thanks to Prof. Katayama of the Tokyo Imperial University, who encouraged him throughout these studies. Sincere thanks are also due to Mr. Katsumi Oeda, who earnestly and incessantly assisted the author in the experiments dealing with very unmanageable and dangerous test substances. Further, the author embraces this opportunity of thanking the Japan Society for the Promotion of Scientific Research, who gave him great assistance for many years and placed at his disposal various kinds of apparatus required in the investigation and of thanking the Saitô Gratitude Foundation, who provided the Research Institute for Iron, Steel and Other Metals with the useful apparatus for obtaining low temperatures.

Cryogenic Section, Research Institute for Iron, Steel and Other Metals, Tôhoku Imperial University.

Studies on Fluorine at Low Temperatures. IX. Experiment on the Reaction between Solid Fluorine and Liquid Hydrogen.

By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

The reaction between fluorine and hydrogen is much complicated. Although close investigations have been made and numerous papers are still being published on the reactions between other halogens and hydrogen in the gaseous state, any systematic study has scarcely been made on the reaction between fluorine and hydrogen. Moreover, strange to say, the results obtained by the few who have studied this problem have been contradictory to one another. For illustrating this fact, the present authors will give the results of their tentative study on the reaction between solid fluorine and liquid hydrogen, and state their own opinion about it.

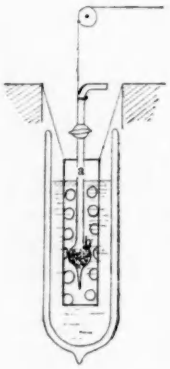
Moissan and Dewar[1] reported that explosion took place when a kind of test-tube with solid fluorine placed on its bottom was dipped into liquid hydrogen and the two elements were brought in contact with each other by breaking the bottom of the tube with a metallic bar thrust in at the upper end of the tube. But Wartenberg[2] and Eyring[3] reported that they saw no remarkable reaction between fluorine and hydrogen at ordinary or low temperatures, though they made no such experiment as Dewar's.

The present authors carried out the following experiments for ascertaining validity of these conflicting reports and the conditions for an explosion of this kind, if any.

I. Experiments and Results. Experiments such as Dewar's, in which, as stated above, a metallic bar is thrust in at the upper end of the tube, have the following drawback: (i) Air may be mixed in the samples, and (ii) it is doubtful whether the hydrogen and fluorine will come in contact with each other respectively in the true liquid and solid states, because the temperature of the metal is probably higher than that of the liquid hydrogen.

(1) Moissan and Dewar, *Compt. rend.*, **136** (1903), 641.
(2) Wartenberg, *Nachr. Ges. Wiss. Göttingen*, **1** (1930), 119.
(3) Eyring, *J. Am. Chem. Soc.*, **55** (1933), 2796.

In the authors' experiment, an apparatus as shown in the figure was used. A brass cylinder was hung in the liquid hydrogen. In this cylinder was also hung a glass bulb containing condensed fluorine. A thread by which the bulb was suspended through a roller was drawn out, and the bulb was dropped. A thin-walled capillary tube of the bulb was broken at the bottom of the cylinder, whereby the solid fluorine and liquid hydrogen touched each other. The following is the summary of the results of experiments:



(1) With an inside diameter of about 10 mm. at a and about 1 c.c. of fluorine in b; the weather cloudy. Immediately after the thread was drawn out and the bulb dropped, a slight explosion was heard and flames were seen on the surface of the liquid hydrogen (surface burning). In about one minute, the Dewar vessel burst, perhaps on account of explosion of the liquid hydrogen (or hydrogen gas) or of thermal strain in the vessel.

(2) With an inside diameter of 1 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Even after the capillary tube was broken, no explosion took place. When the bulb, with the broken capillary tube but still containing the solid fluorine, was taken out, a slight explosion was heard.

(3) With an inside diameter of 6 mm. at a and about 1 c.c. of fluorine in b; exposed directly to the sun. Explosion took place after the breakage of the capillary tube and the Dewar vessel burst shortly after the explosion.

(4) With a diameter of 13 mm. at a and about 1 c.c. in b; exposed directly to the sun. Violent explosion was experienced and even the brass cylinder was crushed.

All these experiments being carried out outdoors and examined at a distance of about 1 metre from the apparatus, the observation might not be very accurate. Nevertheless, a little smoke of light brown colour was seen rising at the opening of the vessel in each case of (1), (3), and (4) after the breakage of the end of the tube.

II. Discussion of the Results. (1) Eyring's denial of the explosion of solid fluorine at the temperature of liquid hydrogen has no ground in experiments. The present authors' experiment was the first to be made after Dewar's investigation. The authors cannot fall in with Eyring's views that there is no explosion between solid fluorine and liquid hydrogen, and that the explosion, if any, is caused by contaminating

organic matters (Eyring admitted explosion of a mixture of hydrogen gas and fluorine gas at an ordinary temperature, but attributed it to organic matters such as rubber). In the authors' experiment, grease or other organic matters were not used.

(2) Explosion did not always occur. With a capillary tube as used in experiment (2), no explosion took place.

(3) The explosion was more frequent and violent with a tube having a larger diameter. In the authors' opinion, the reaction in question may be one not between the solid and liquid but in the gas phase existing over the solid and liquid, thus resulting in the above-mentioned explosion.

(4) No explosion, however, was experienced when the gases of the two elements were mixed in a large glass vessel at ordinary temperature —even when the vessel was exposed to the sun or to the light of a mercury lamp. (Explosion sometimes occurred when the wall of the vessel was fresh.) If so, how is the explosion at such a low temperature explained? The following questions arose in the authors' mind:

(a) Does a condensed gas become chemically more active when it is liquefied or vaporized?

(b) Is there any transition into an active form in solid fluorine at this temperature?

(c) Does any negative catalyser exist in this reaction in the gas phase? Can the explosion not be explained by degeneration at low temperature of the negative catalyser?

As for (a), fluorine fresh from the electrolyser was found, in the authors' experiment, more apt to chemical reaction than one which was first liquefied and condensed and then vaporized, but there was no ground for answering (a) in the negative.

As for existence of the transition referred to in (b), although there was a slight change in the colour of the solid fluorine at the temperature of the liquid hydrogen, such is also the case with other halogens. Determination of the molecular heat showed no transition.

As for degeneration of a negative catalyser, the results of the authors' investigation on the reaction of gases $H_2 + F_2 \rightarrow 2HF$ have shown that this reaction is greatly affected by the wall of the vessel used, and have pointed to the probability of negative catalysis of SiF_4 coming from the glass wall. It may also be conceived that a negative catalyser of this kind will completely freeze and will degenerate at such a low temperature as that of liquid hydrogen.

The foregoing, however, is a mere supposition, and the authors cannot give any definite opinion about the reaction in these seemingly heterogeneous phases until the reaction between hydrogen and fluorine in the gas phase is thoroughly investigated.

The authors wish to express their heartful thanks to the Japan Society for the Promotion of Scientific Research for a grant.

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Studies on the Aqueous Solutions of Some Chromic Salts. II. Modified Green Chromic Sulphate, Ol Green Chromic Chloride and Green Chromic Sulphate.

By Hideo SUEDA.

(Received October 12th, 1937.)

I. Modified Green Chromic Sulphate. When the aqueous solution of the violet chromic sulphate is boiled for two or three minutes, the colour of the solution changes to green and retains the colour even after it is cooled. The compound which is prepared from the violet sulphate in such a manner is generally called "modified green chromic sulphate". Many researches have already been reported on this compound. From the thermochemical point of view, A. Recoura[1] discovered the formation of sulphuric acid at the rate of one molecule per four chromium atoms in the solution, when the violet sulphate was transformed into this compound. Before Recoura, P. A. Favre and C. A. Valson[2] observed that one-third of the sulphate radical was precipitated by addition of barium chloride in the freshly prepared modified green sulphate solution. A. Recoura, having combined his results with this experiment, recognized that the following equation explains the reaction when the violet sulphate solution is heated. He gave therefore formula $[Cr_4(SO_4)_4O]SO_4$ to the modi-

(1) *Bull. soc. chim.*, [3], **9** (1893), 586; [3], **15** (1896), 315; *Ann. chim. phys.*, [7], **4** (1895), 494.

(2) *Compt. rend.*, **74** (1872), 1023.

fied green chromic sulphate. W. R. Whitney[3] also supported this idea after his measurement of the electric conductivity of this salt.

$$2Cr_2(SO_4)_3 + H_2O = [Cr_4(SO_4)_4O]SO_4 + H_2SO_4$$

After that, H. G. Denham[4] measured the *p*H-value of the solution in various dilutions, and the molecular weight of the salt was shown to be double or more that of the violet sulphate. Taking the experimental results proposed by T. W. Richards and F. Bonnet[5] as his idea, he assumed the formula $[Cr_4(SO_4)_4](SO_4)_2$ for this salt, and the hydrolysis of this salt in the solution was expressed according to its concentration as follows:

$$[Cr_4(SO_4)_4](SO_4)_2 + 2H_2O \rightleftarrows [Cr_4(SO_4)_4]SO_4(OH)_2 + H_2SO_4 \quad (1),$$

$$[Cr_4(SO_4)_4](SO_4)_2 + 4H_2O \rightleftarrows [Cr_4(SO_4)_4](OH)_4 + 2H_2SO_4 \quad (2),$$

where the reaction of equation (1) takes place in such a concentration as that experimented on by Recoura, while equation (2) is suitable for a very dilute solution. This consideration enabled him to explain his experiment, and his idea seems nowadays to have been generally adopted.

But, the complex ion $[Cr_4(SO_4)_4]^{4+}$ is not easily deduced from Werner's co-ordination theory, and there are some questions on the number of chromium atoms in the complex radical. The salt $[Cr_4(SO_4)_4](SO_4)_2$ which Denham assumed, should be obtained, according to his idea, when the infinitely concentrated violet sulphate solution is heated. But the compound, which is actually produced when the crystals of violet sulphate hydrate are heated, is difficultly soluble in water, contrary to the expectation from Denham's idea. Such circumstances tempted the author to study this compound.

(1) *Relation between the concentration of the modified green sulphate and the quantity of the sulphate ion precipitable by barium chloride.* According to Denham, the complex ion of the modified sulphate $[Cr_4(SO_4)_4]^{4+}$ is not changed, whatever the concentration of the solution may be. If so, the total quantity of the sulphate radical should be three times the quantity of the sulphate ion to be precipitated by barium chloride in any concentration. As the experimental proof of it was wanting, the author has determined the quantity of barium sulphate produced on adding concentrated barium chloride to the solutions in three different

(3) *Z. physik. Chem.*, **20** (1896), 40.
(4) *Z. anorg. allgem. Chem.*, **57** (1908), 361.
(5) *Z. physik. Chem.*, **47** (1904), 29.

concentrations prepared by immediate cooling after boiling violet sulphate for three minutes, i.e. 0.06, 0.005 and 0.0006 mol/l. (molecular formula of violet sulphate being $Cr_2(SO_4)_3 \cdot 17H_2O$). The ratio of the precipitated sulphate ion to the total sulphate radical are shown in Table 1.

Table 1.

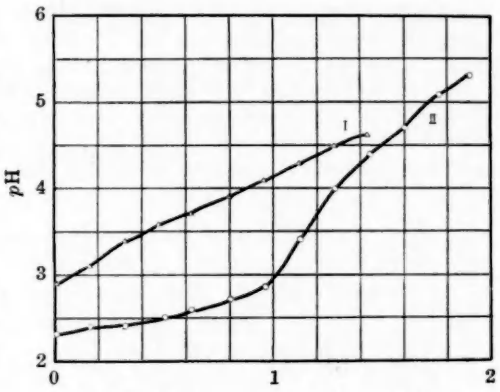
Conc. of the solution (mol/l.)	0.06	0.005	0.0006
Precipitated sulphate (%)	34.6	50.5	64.6

These results show that the percentage of sulphate ion depends on the concentration of the solution, and cannot be deduced from Denham's idea. In other words, the concentration of the solution controls the quantity of the sulphate radical in the complex ion of the modified green sulphate, and the quantity was between one-third and two-thirds of the total sulphate in the range of these concentrations.

(2) *The relation between the concentration of the solution and the quantity of sulphuric acid formed in the solution.* As described above, Recoura and Whitney showed that one molecule of sulphuric acid was liberated for four chromium atoms, when the violet sulphate was transformed into the modified sulphate. The concentrations of the solutions employed by them were moderately great, i.e. 1/12 and 1/30 mol/l., and the case of a smaller concentration has not yet been studied. The present author has examined such a case. Electrometric titration has been applied for this purpose, by using the antimony electrode[6]. A sodium hydroxide solution was added to 1/200 mol/l. violet and modified green sulphate solutions. The latter green sulphate solution was prepared from the former violet sulphate solution by the usual method. The titration curves are shown in Fig. 1. The curve of violet sulphate (I) smoothly rises, while that of modified green sulphate (II) begins at a lower *pH*-value than curve I, the increase of *p*H is not considerable till the molecular ratio of sodium hydroxide and chromic sulphate becomes equal, and it becomes noticeable after the point of equilibrium is passed. This result shows that one sulphuric acid molecule is liberated for four chromium atoms, even when a modified sulphate is formed in such a dilute solution. As described in (1), the relative quantity of sulphate ion increases when the

(6) T. Uemura and H. Sueda, this Bulletin, **8** (1933), 1.

concentration of the solution changes from 6/100 to 1/200 mol/l., but the relative quantity of the liberated sulphuric acid is independent of the concentration of the solution.



Molecular ratio [NaOH] : [$Cr_2(SO_4)_3$]

I: Violet chromic sulphate.
II: Modified green chromic sulphate.

Fig. 1.

(3) *Absorption spectra.* The absorption spectra, given by the following six solutions, were measured with the concentration of 1/100 N: (a) solution immediately cooled after heating, (b) solution prepared to *p*H 1.0 by adding sulphuric acid, (c) solution standing for 24 hours, (d) solution standing for several days, (e) solution in which the liberated sulphuric acid was neutralised with sodium hydroxide, and (f) solution in which the sulphate ion was removed by filtering off barium sulphate after the addition of the equivalent amount of barium chloride. These solutions show similar curves which can be represented by one curve (I in Fig. 2). Curve I compares with that given by $[Cr(H_2O)_5OH]Cl_2$, but the absorption capacity of the former is higher than that of the latter in shorter wave length. The absorption of the modified sulphate solution does not show any change by the addition of acid, while the colour of the hydroxo-pentaquo chromic chloride solution becomes bluish violet. The properties of these two salts were

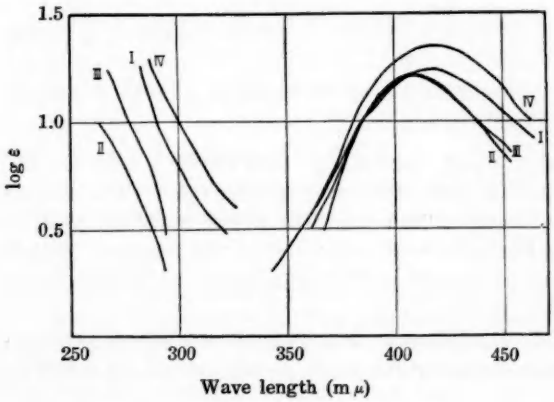


Fig. 2.

essentially different at this point, and the author cannot accept the idea of H. T. S. Britton[7].

As an addition of acid to the modified green chromic sulphate solution does not influence the absorption, the compound must be ol-salt. The removal of sulphate ion or the neutralisation of the liberated acid does not show any effect nor does it change the curves, so they are independent of the complex ion.

(4) *Constitution of the modified green chromic sulphate.* Denham considered that the modified sulphate should contain four chromium atoms in its complex radical. This consideration came from his confirmation that the molecular weight of its cation could be double that of violet sulphate which was assumed as $[Cr_2--]^{6+}$. As the author, however, indicated in the previous paper that the cation of violet sulphate should be $[Cr(H_2O)_6]^{3+}$, the cation of modified sulphate must be considered to contain two chromium atoms, since it has about double the molecular weight of $[Cr(H_2O)_6]^{3+}$.

It has been shown that in (1) one-third of the sulphate radical of modified sulphate can be found as ion in the solution of 6/100 mol/l., but when the concentration decreases to 6/10000 mol/l., the quantity of the sulphate ion becomes two-thirds of whole sulphate radical, while in (2) ratio of the liberated sulphuric acid to the chromium atom does not show any relation with its concentration, that is, one sulphuric acid molecule is produced for four chromium atoms, and in (3) the modified green sulphate must be ol-compound. After all, the author considers the following schema for the formation of the modified green sulphate:

$$2[Cr(H_2O)_6]_2(SO_4)_3 \longrightarrow [(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3]_2SO_4 + H_2SO_4$$

(concentrated solution, about 6/100 mol/l.),

$$2[Cr(H_2O)_6]_2(SO_4)_3 \longrightarrow [(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]_2(SO_4)_3 + H_2SO_4$$

(dilute solution, about 6/10000 mol/l.),

and when the concentration of the solution is intermediate between the above-mentioned, a mixture of both salts can be obtained. The reason for giving the μ-sulphato form to the modified green sulphate will be explained later. The number of water molecules in the complex radical has been selected in order to comply with the demand of Werner's co-ordination theory.

(5) *Relation between the time of standing of the modified green chromic sulphate and the quantity of the sulphate radical precipitated by*

(7) *J. Chem. Soc.*, **127** (1925), 2120.

barium chloride. As mentioned above, 50.5% of the sulphate radical was precipitated by barium chloride in the fresh modified sulphate solution, but after standing for 24 and 130 hours, 53.6 and 59.1% of sulphate could be respectively precipitated. This shows that the sulphate radical in the complex radical decreases proportionally to the time of standing of the solution. This can be expressed as follows:

$$[(H_2O)_5Cr(OH)(SO_4)_2Cr(H_2O)_5]^+ \ (1) \longrightarrow [(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4]^{3+} \ (2).$$

From the quantity of the sulphate ion in the fresh solution, the ratio of the quantity of compound (1) to that of (2) should be 1:1.07, while it becomes 1:3.44 after standing for 130 hours. In spite of such a change, the absorption spectra do not differ. This result cannot be explained unless the absorption spectra of these two compounds are quite similar.

II. Ol Green Chromic Chloride. As described in the previous section, when the colour of the violet chromic sulphate solution is once changed to green by heating, the latter colour does not easily change even at a low temperature. But, the violet chromic chloride solution returns to bluish violet, in proportion to the depression of the temperature, though it is green in the hot state producing $[Cr(H_2O)_5OH]Cl_2$ according to Bjerrum[8]. It is very interesting to note that sulphate and chloride behave differently in spite of the same cation[9]. The author already published a paper[10] of an analogous example, i.e. diaquo-tetrammine-cobaltic sulphate changes to ol-compound by the addition of an alkali, while the corresponding chloride has not a similar reaction.

Although the violet chromic chloride solution changes reversibly by heating and cooling, the hydroxo-pentaquo-chromic chloride solution given by adding equivalent sodium hydroxide to violet chloride solution does not return to the original hydroxo-compound when it is cooled after heating, but is transformed into another salt which is called, in this paper "ol green chromic chloride".

(1) *Absorption spectra.* Absorption spectra of the four following solutions were observed: (a) solution prepared by cooling immediately

(8) *Z. physik. Chem.*, **59** (1907), 339.

(9) Violet nitrate solution behaves similarly to chloride: it returns to bluish violet after cooling. According to H. Brinzinger and F. Jahn, *Z. anorg. allgem. Chem.*, **229** (1936), 410, $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$ are transformed into "zweischalige" complex salts $[[Cr(NH_3)_6](SO_4)_4]^{5-}$ and $[[Cr(en)_3](SO_4)_4]^{5-}$ by ammonium sulphate, but ammonium nitrate cannot transform them into the salts of this kind.

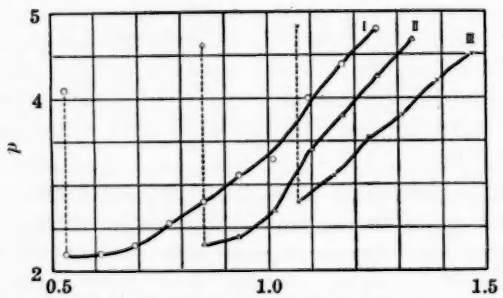
(10) This Bulletin, **10** (1935), 50.

after boiling 1/100 mol/l. violet chloride $[Cr(H_2O)_6]Cl_3$ solution for two or three minutes (curve II in Fig. 2), and (b) solution obtained by treating 1/100 mol/l. green chloride $[Cr(H_2O)_4Cl_2]Cl$ similarly as above (curve III). As these two curves are similar to that of violet chloride, it can be said that this violet chloride at least predominated in the solutions then obtained. Their *p*H-values do not change before and after heating . (c) 1/100 mol/l. violet chloride solution was prepared by using 1/100 N sodium hydroxide as solvent (precipitation then occurred but was dissolved by heating the solution), and it was heated to boiling and then cooled immediately. (d) Solution obtained by adding concentrated hydrochloric acid to solution (c) to *p*H 1.1.

As solutions (c) and (d) show similar absorption spectra, they can be represented by one curve (curve IV in Fig. 2) which is different from that given by hydroxo-pentaquo salt. As solution (c) showed no different absorption on the addition of acid, an ol-compound must be assumed to be produced when the solution of $[Cr(H_2O)_5OH]Cl_2$ was heated.

(2) *Potentiometric titration.* To confirm that the "ol green chromic chloride" is actually an ol-compound, and to determine the number of OH in the complex radical in case of ol-compound, potentiometric titration was applied after heating and immediately cooling the solutions, where violet chloride and sodium hydroxide was mixed in various proportions.

When the violet chloride was dissolved to 1/100 mol/l. in 0.0053 N sodium hydroxide, the resulting solution showed *p*H 4.1, but *p*H 2.2 after heat treatment[11]. The solution was then titrated with sodium hydroxide, the titration curve being indicated in Fig. 3 (curve I). The solutions, where the molar ratios of violet chloride to sodium hydroxide were respectively 1.00 to 0.85 and 1.00 to 1.07, showed *p*H 4.6 and 4.8 before heating. The *p*H-values, however,



Molecular ratio $[NaOH] : [Cr(H_2O)_6]Cl_3$

Fig. 3.

(11) This was done as in the case of preparing the modified sulphate from the violet sulphate.

changed to 2.3 and 2.8 respectively after heat treatment. The titration curves are shown in Fig. 3 (curve II and III respectively). This decrease of *p*H-value of the solution of violet chloride with sodium hydroxide after heat treatment must be due to the formation of ol-compound. The change in inclination of the titration curve suggested that the number of OH contained in the complex radical is equal to that of the chromium atoms in the radical.

(3) *Constitution of the ol green chromic chloride.* Bjerrum's "latent basic salt"[12] perhaps corresponds to ol green chromic chloride discussed in this paper. But as the preparation method is somewhat different from Bjerrum's, it is probably vain to compare these two compounds[13].

In (1) and (2), it has been proved that "ol green chromic chloride" is an ol-compound, and the number of OH and that of the chromium atoms in the complex radical are equal. In order to examine the existence of the chlorine atom in the radical, an excess of silver nitrate was added to cold solution of this salt, and the quantity of immediately precipitated silver chloride was measured. As all chlorine atoms was then precipitated, they cannot be contained in the complex radical. Summarising the facts observed, the author considers the following equation for the formation of this salt and gives it the formula shown below:

$$Cl_2[(H_2O)_5CrOH] + [OHCr(H_2O)_5]Cl_2 \rightarrow [(H_2O)_4Cr(OH)_2Cr(H_2O)_4]Cl_4 .$$

The author has not yet obtained any confirmation that this salt contains two chromium atoms in its complex radical. But such has been deduced from the two following points: (i) Pfeiffer[14] already proved the formation of $[(en)_2Cr(OH)_2Cr(en)_2]X_4$ on heating $[Cr(en)_2H_2OOH]X_2$, and (ii) the salt produced by heating the violet sulphate is di-chromium salt and the absorption spectra of the di-chromium salt is somewhat similar to that of this salt. According to Werner's co-ordination theory, eight molecules of water must exist in the complex radical in this case. Instead of ol-compound, the salt in question can be assumed to be oxo-compound which is closely related with ol-compound. But in general ol-compound is difficultly transformed into oxo-compound, except by heating or by standing for a long time. It may therefore be reasonable to take the ol-combination in this case.

(12) *Z. physik. Chem.*, **59** (1907), 336, 581; **73** (1910), 724; N. Bjerrum and C. Faurholt, *ibid.*, **130** (1927), 585.

(13) Properties of the salt depend on the method of preparation, as Bjerrum has pointed out in his papers.

(14) *Z. anorg. allgem. Chem.*, **56** (1908), 261.

III. **Green Chromic Sulphate $[Cr_2(SO_4)_3(H_2O)_3]$ and $[Cr_2(SO_4)_3(H_2O)_6]$.** When violet sulphate is heated in aqueous solution, a modified green chromic sulphate, i.e. μ-ol-mono- or di-sulphato-dichromic sulphate is produced, but when it is heated in a crystalline state at 90°C., it changes into the green chromic sulphate $[Cr_2(SO_4)_3(H_2O)_3]$[15]. This green sulphate cannot be rapidly dissolved in water. It took about 100 minutes to dissolve 2 g. of this salt in 500 c.c. of water at 25°C. with constant stirring. The fresh solution so obtained shows an absorption analogous to that given by the solution of $[Cr_2(SO_4)_3(H_2O)_6]$[15], and neither solution gives immediately a precipitate of barium sulphate on the addition of barium chloride. These two salts, therefore, become the same substance in solution.

The quantity of the sulphate radical, that is precipitable by barium chloride, increases proportionally to the time of standing. In order to explain this fact, A. Colson[16] assumed three types of green chromic sulphate from his thermochemical studies: (a) all sulphate radicals, (b) two-thirds and (c) one-third, are masked in the complex radical:

$$[(H_2O)_3Cr(SO_4)_3Cr(H_2O)_3] \rightarrow [(H_2O)_4Cr(SO_4)_2Cr(H_2O)_4]SO_4$$
$$\rightarrow [(H_2O)_5Cr(SO_4)Cr(H_2O)_5](SO_4)_2 \quad (1).$$

On the other hand, he considered that $[Cr_2(SO_4)_3(H_2O)_6]$ is in equilibrium with the modified green chromic sulphate in aqueous solution:

$$[(H_2O)_3Cr(SO_4)_3Cr(H_2O)_3] \rightleftarrows [(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3]SO_4H$$
$$\rightleftarrows [(H_2O)_3Cr(OH)_2(SO_4)Cr(H_2O)_3](SO_4H)_2 \quad (2).$$

The relation between these two schemata is not clear to the present author. After taking the absorption spectra, the author studied to know which of these schemata should be taken in this case, and, besides, examined some reactions of the solution with alkali and in heat treatment.

(1) *Relations found on leaving the aqueous solution of the green chromic sulphate to stand.* 1/112 mol/l. green chromic sulphate solutions was kept for 10 min., 245 min., 25.5 hours and 90 hours after the salt was completely dissolved, and their absorption spectra were observed. The absorption spectra of the first two solutions (10 min. and 245 min.) are similar to each other and are represented by one curve in Fig. 4 (curve I), and the other two solutions gave also analogous absorption curves, which

(15) A. Sénéchal, *Compt. rend.*, **159** (1914), 243.

(16) *Bull. soc. chim.*, [4], **1** (1907), 438, 889; **3** (1908), 90; *Ann. chim. phys.*, [8], **12** (1907), 433.

are represented by another curve (curve II in Fig. 4). The absorption spectra of the modified green chromic sulphate is given as curve III. If the schema (2) can express the reaction which occurs on leaving the aqueous solution of green chromic sulphate to stand, the production of the modified sulphate being recognised, curve II should come between curve I and III. However, curve II is found to be outside the other two in the ranges of wave lengths below 300 mμ and above 410 mμ. The *p*H-value does not change on standing, and remains at 2.5. For these reasons, the author believes this reaction must be explained by schema (1) but not by (2).

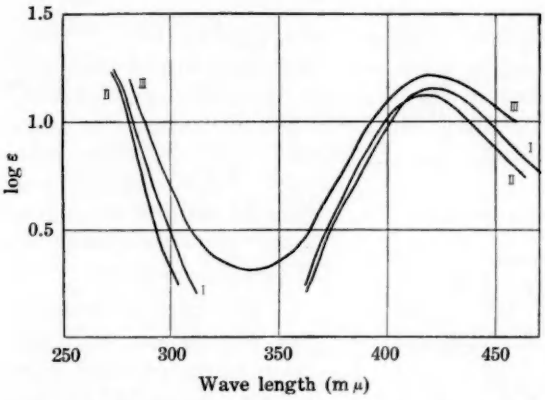


Fig. 4. The absorption spectra of green chromic sulphate.

After standing for 60 minutes and 75 hours, 1/200 mol/l. solutions of the salt precipitated respectively 14.9 and 54.6% of the sulphate radical on the addition of barium chloride. The precipitation of barium sulphate cannot be observed in the fresh solution, so the reaction $[Cr_2(SO_4)_3(H_2O)_6] \rightarrow [Cr_2(SO_4)_2(H_2O)_8]SO_4$ is assumed to take place rapidly as compared with the reaction $[Cr_2(SO_4)_2(H_2O)_8]SO_4 \rightarrow [Cr_2(SO_4)(H_2O)_{10}](SO_4)_2$. $[Cr_2(SO_4)_3(H_2O)_6]$ and $[Cr_2(SO_4)_2(H_2O)_8]SO_4$ can be assumed to exist in different ratios in the solutions after standing for 10 min. and 245 min., but their absorptions are alike. This must be caused by the originally similar absorption of the two salts. In this case, as well as in the case of modified green chromic sulphate, it seems that the absorptions were not much influenced, whether the chromium combination in the radical be with two bridges or three.

(2) *Reaction with alkali.* Sodium hydroxide was added to the solutions of green chromic sulphate, which were left for 110 minutes and 90 hours respectively, in order to make the molecular ratio $[Cr_2(SO_4)_3(H_2O)_6] : [NaOH] = 1.00 : 1.26$. The *p*H-values were the same and 4.2. Both solutions gave similar absorption curves represented by curve III in Fig. 4, and the curve is similar to that given by the modified

green chromic sulphate. From this result, it is evident that when the green sulphate solution is left for a time, the modified sulphate is obtained by the addition of sodium hydroxide. However, potentiometric titration is necessary to confirm it.

1/200 mol/l. green sulphate solutions were titrated with 8/100 N sodium hydroxide after standing for 3 hours and 75 hours respectively. The titration curves are shown in Fig. 5 (curve I and II). Next, sodium hydroxide was added to the solution, which was left for 75 hours, to make the molecular ratio $[Cr_2(SO_4)_3(H_2O)_6]$: [NaOH]=1.0 : 1.6. The solution then obtained was titrated with hydrochloric acid, and the result is shown by curve III.

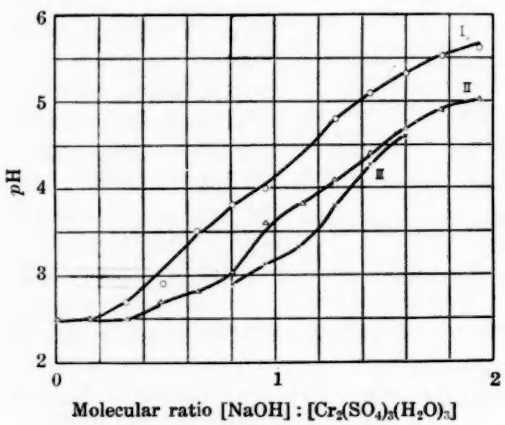


Fig. 5.

The time of standing has no relation with *p*H-value of the solution, when sodium hydroxide is not added (*p*H=2.5). This shows that ol-compound or free acid is not produced by standing. Titration curves (I and II) do not so rapidly rise at the beginning of the process, and this is explained by assuming that a part of the green sulphate is converted into ol-compound when sodium hydroxide is added to the solution. This assumption is also confirmed by the disagreement of curves II and III. In conclusion, the green sulphate is transformed into the modified sulphate in aqueous solution by the addition of sodium hydroxide. This is the reason why the author assumed the sulphato-bridge in the formula of the modified sulphate. As shown in Fig. 5, the elevation of curve I begins earlier than that of curve II, and this means that $[Cr_2SO_4(H_2O)_{10}](SO_4)_2$ can more easily be converted into ol-compound than $[Cr_2(SO_4)_2(H_2O)_8]SO_4$ or $[Cr_2(SO_4)_3(H_2O)_6]$.

(3) *Reaction in heat treatment.* The heat treatment[11] was performed with 1/200 mol/l. solutions, which had been left for 10 minutes and 75 hours respectively. The absorption curves given by these solutions thoroughly coincide with curve III in Fig. 4.

Titration curves of the solutions are shown in Fig. 6, where curves I and II respectively belong to the solutions left for 3 hours and 75 hours. These curves are analogous to that of modified green sulphate (Fig. 1).

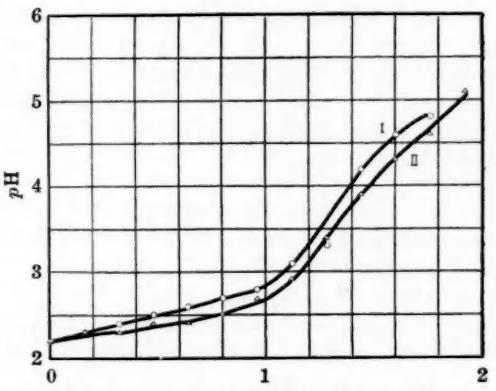


Fig. 6.

The author next measured the quantity of sulphate radical which can be precipitated by barium chloride, and obtained the results summarised in Table 2. As for the solution left for one hour, the precipitated sulphate radical is smaller before the heat treatment, but it becomes larger after treatment, and for the solution left for 75 hours, this relation is quite contrary. The disagreement between the quantities of the precipitable sulphate radical obtained from these two solutions after heat treatment, comes perhaps from the difference of the heating intervals, and the values are approximately that obtained from the modified sulphate (50.5%). Hence, modified green chromic sulphate can always be obtained by heating the green chromic sulphate in aqueous solution.

Table 2. Quantity of the precipitated sulphate radical (%).

Time after dissolution	1 hour	75 hours
Before heat treatment	14.9	54.6
After heat treatment	53.9	47.4

Summary.

(1) For the modified green chromic sulphate, the formula μ-ol-mono- or di-sulphato-di-chromic sulphate has been deduced (i) from its absorption spectra, (ii) from the quantities of sulphuric acid produced

when this salt is formed from violet chromic sulphate, and (iii) from the sulphate ions which is precipitated by barium chloride in various dilutions.

(2) When hydroxo-pentaquo chromic chloride solution was heated, the author recognized the production of ol-compound, to which the formula di-ol-octaquo-di-chromic chloride has been given.

(3) The modification of the green chromic sulphate in aqueous solution, produced on standing, or on heating, or on adding sodium hydroxide, has been discussed.

In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

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Über das durch Zersetzen von Schwefelwasserstoffwasser hergestellte disperse System von Schwefel und dessen Reaktion mit dispersem Quecksilber.

Von Naoyasu SATA.

(Eingegangen am 26. November 1937.)

I. Einleitung. Dass das H_2S-Wasser oder der H_2S unter Vorhandensein von Wasserdampf, thermisch zersetzt wird und bläuliche Flüssigkeit mit weisser Trübung ergibt, ist schon seit C. Geitner,[1] A. Gautier[2] usw. beobachtet worden. Obwohl diese Forscher diese Flüssigkeit als ein kolloid-disperses System von Schwefel aufmerksam gemacht hatten, fehlt noch weitere Untersuchung von kolloidchemischem Standpunkt aus. Ich habe zufälligerweise gefunden, dass beim Zuschmelzen eines H_2S-Wasser haltendes Probierglases ein ähnlicher Vorgang vor sich läuft; nämlich nach dem Zuschmelzen das H_2S-Wasser zu einer weiss trübe, bläulich opaleszierenden Flüssigkeit umgewandelt wird. Eingehende Untersuchung hat gezeigt, dass sie eine Art hydrophobes

(1) C. Geitner, *Ann.*, **129** (1864), 364.
(2) A. Gautier, *Compt. rend.*, **142** (1906), 1469.

Schwefel-Sol ist, wie Weimarnsches Sol[3] oder durch Explosionsmethode hergestelltes Sol.[4] Da die Herstellungsweise so einfach und praktisch ist wurde einige Eigenschaften dieses Sols, sowie die Reaktion von demselben mit dispersem Quecksilber im folgenden behandelt.

II. **Die Methodik.** Zum Zweck der Vorlesungsdemonstration ist es sehr einfach und zwar erfüllt man etwa 1/3 von einem Probierglas mit H_2S-Wasser und schmilzt es zu, unter Berücksichtigung das Erhitzen der Flüssigkeit möglichst zu vermeiden. Der H_2S in der Nähe der Schmelzstelle wurde unter Vorhandensein genügender Wasserdämpfe thermisch zersetzt und scheidet das Schwefel in dispersem Zustand aus. Während sowie nach dem Zuschmelzen, ersieht man milchweisse Flüssigkeit an der Innenwand des Probierglases herunterströmt, welche beim Zusammenmischen mit H_2S-Wasser ein weiss trübes, bläulich opaleszierendes System ergibt. Dieses Sol, wie die andere von hydrophober Natur, ist nicht sehr beständig und fängt nach dem Entstehen gleich an zu koagulieren und absetzen. Während dieses Stadiums, zeigt das System genau denselben polychromische Verlauf, wie die andere Sole nach Weimarn bzw. Auerbach[5]. Neue Methode ist dadurch bevorzugt, dass es dabei keine besondere Vorbereitung an Reagentien verlangt wird, wie z.B. Lösungen bestimmter Konzentrationen vorzubereiten, Mengenverhältnis der Reaktionsflüssigkeiten zu berücksichtigen usw. wie bei den anderen Methoden.

Zum Herstellen grösserer Menge empfehlt es sich, als Reaktionsgefäss, ein enghalsiges Kolben, wie z.B. ein Messkolben, benutzen. Am besten habe ich ein Quarz-Messkolben genommen, welches etwa bis zur Hälfte H_2S-Wasser enthält, wie in Abb. 1 skizziert ist. Wenn man an den Hals des Kolbens stark erhitzt, wird die Flüssigkeit bläulich, bläulich weiss opaleszierend und endlich milchweiss mit rötlicher Durchsichtsfarbe. In der Literatur wurde hingewiesen, dass die Schwefelsäure bei diesem Zersetzen entstehen würde[1][2][6]. Aber nach meinem Versuch lässt die Schwefelsäure, weder mit $BaCl_2$-Lösung noch an Lackmuspapier, sich nachweisen.

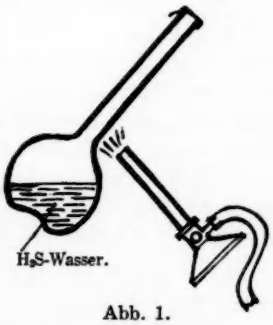
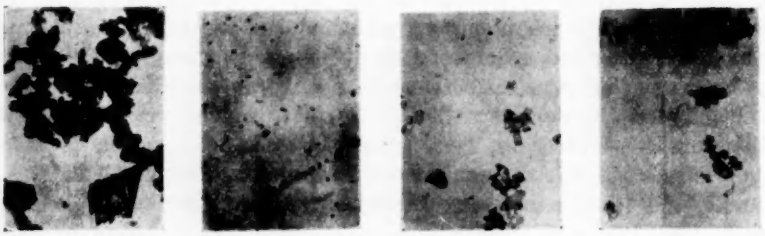


Abb. 1.

(3) P. P. von Weimarn und B. W. Malyschew, *Kolloid-Beihefte*, **8** (1911), 216.
(4) P. P. von Weimarn und N. Sata, *Kolloid-Z.*, **66** (1934), 1; N. Sata, dieses Bulletin **11** (1936), 501.
(5) R. Auerbach, *Kolloid-Z.*, **27** (1920), 223.
(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Bd. X, 130, London (1923).

III. Der Absetzungsvorgang des dispersen Systems und die mikro- und ultramikroskopische Untersuchung des Sedimentes. Von dem dispersen System, wie erwähnt hergestellt ist, wurde der übrig gebliebene H_2S durch Kochen bzw. durch Bestrahlen von USW.[7] ausgetrieben. Die Absetzungsvorgänge der dispersen Systeme und die Resultate der mikro- und ultramikroskopischen Untersuchungen der Sedimente sind in folgender Tabelle 1, Abb. 2-a, 2-b, 2-c und 2-d zusammengestellt.



(a) (b) (c) (d)

Abb. 2. (Vergrösserung = 305×)

Von den Versuchsergebnissen, möchte ich auf folgenden Punkte aufmerksam machen.

(1) *Einfluss von Kochen.* Beim Vergleich der Probe (a) und (c) in der Tabelle 1, ersieht man, dass zum Absetzungsvorgang das Kochen kaum einen Einfluss auszuüben ist. Aber die mikro- und ultramikroskopische Untersuchung lässt sich bedeutenden Unterschied zwischen ihnen erkennen; nämlich scheidet die Probe (a) (H_2S-haltiges Präparat) viel grössere Kristalle als (c) (durch Kochen H_2S ausgetriebenes Präparat) aus. Daraus könnte man konstatieren, dass im vorigen Fall sich der H_2S allmählich zersetzte und dadurch ausgeschiedener Schwefel zu grösseren Kristallen angehäuft hatte.

(2) *Wirkung von USW.* Die Wirkung von USW. auf dem dispersen System ist besonders bemerkenswert. Die Mikro-Aufnahme des Sedimentes von USW.-bestrahltem Präparat (b) gibt ein eigenartiges Bild, wie aus der Abb. 2-b ersichtlich ist. Darauf ist es deutlich zu erkennen, dass die grössere Kristalle darin ganz und gar ausfallen und nur verhältnismässig kleine Kriställchen in ausserordentlich gleichmässiger Dimension ausgeschieden sind. Das könnte man vielleicht so erklären,

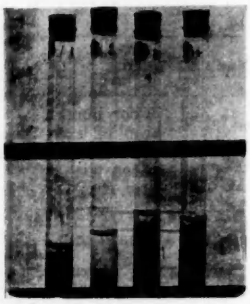
(7) Abkürzung von Ultraschallwellen; über Entgasung durch USW., siehe L. Bergmann, "Der Ultraschall", 178, Berlin (1937); G. Schmid, *Angew. Chem.*, **49** (1936), 117.

Tabelle 1.

<table>
<tr><th></th><th>a</th><th>b</th><th>c</th><th>d</th></tr>
<tr><td>Behandlung.</td><td>H_2S-haltig. (Kontrolle)</td><td>USW. bestrahlt für 1 Min.</td><td>2 Min. gekocht.</td><td>2 Min. gekocht u. dann 1 Min. USW.</td></tr>
<tr><td>Anfangs.</td><td>Milchweiss trübe und fast undurchsichtig; Durchsichtsfarbe ist organe-rot.</td><td>Trübung und Farbton ist genau wie (a); riecht noch schwach nach H_2S.</td><td colspan="2">Milchweiss trübe, ganz undurchsichtig; riecht vollkommen nicht nach H_2S.</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Nach 1 Tag: 1 mm. von oben ist ganz klar u. unten undurchsichtig wie (a).</td></tr>
<tr><td>Nach 1 Tag.</td><td>1 mm. von oben ist ganz klar; unten undurchsichtig.</td><td>Setzt schon halbdurchsichtig ab.</td><td colspan="2">Nach 3 Tagen.</td></tr>
<tr><td>Nach 3 Tagen.</td><td>1/2 von oben ist fast klar; unten noch weiss trübe mit violetter Durchsichtsfarbe.</td><td>Setzt fast ganz klar ab.</td><td>1/2 von oben ist fast klar und unten weiss trübe wie (a).</td><td>1/2 von oben ist bläulich klar mit Opaleszenz; unten wie (a) bzw. (c).</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Nach 6 Tagen.</td></tr>
<tr><td>Nach 6 Tagen.</td><td>Fast ganz klar.</td><td>Ganz klar.</td><td rowspan="2">Fast ganz klar. Durch Hand-Schütteln nicht peptisierbar.</td><td rowspan="2">Flüssigkeit ist bläulich opaleszierend. Das System ist durch Hand-Schütteln wieder milchweisses, in Durchsicht rotes Sol peptisierbar.</td></tr>
<tr><td>Nach dem Absetzen.</td><td colspan="2">Durch Hand-Schütteln nicht wieder peptisierbar u. setzen sofort ganz klar ab.</td></tr>
<tr><td>Mikro- und ultramikroskopischer Befund der Sedimente.</td><td>Sediment besteht grobe Kristallen in verschiedenen Formen (Platten, Prismen, Nadeln, Oktaedern, Kügeln usw.) aus. Ultramikroskopische Teilchen sind sehr wenig u. fast keine in Brownscher Bewegung. (Siehe Abb. 2-a)</td><td>Fehlt hier die grössere Kristalle vollkommen aus und nur kleine Kristalle in ähnlicher Grösse sind vorhanden. Ultramikroskopische Teilchen sind mehr als in (a), die aber kaum in Brownscher Bewegung sind. (Siehe Abb. 2-b)</td><td>Kristalle in verschiedener Formen u. Grössen, wie in (a) sichtbar. Sie sind aber durchschnittlich kleiner als in (a) u. bedeckt mit ultram kroskopischen Teilchen. Ausserdem ziemlich viele Teilchen sind in Brownscher Bewegung. (Siehe Abb. 2-c)</td><td>Mikroskopischer Befund ist fast genau wie (c), aber die ultramikroskopische Teilchen sind alle in lebhafter Brownschen Bewegung. (Siehe Abb. 2-d)</td></tr>
</table>

dass die innere Schwankung der Konzentration des Systems durch Anregung der USW. ausgeglichen wurde und ein gleichmässiges Erwachsen der Kristallkeime hervorgerufen hat. Da die USW. bekanntlich an der Grenzfläche "flüssig/fest" besonders kräftig wirken,[8] ist es auch sehr möglich, dass sie auf der Oberfläche der Kristallkeime etwaigen Einfluss gegeben hatten, welcher das gleichmässige Kristallwachstum verursachen würde. Dass die einzelne Kristalle klein sind, könnte davon kommen, weil der grösste Teil von H_2S durch USW.-Bestrahlen ausgetrieben worden war.

(3) *Über die Beständigkeit des dispersen Systems.* Zuletzt möchte ich noch über die Beständigkeit etwas hinzufügen. Hierbei ist es auch zu beachten, dass das USW.-bestrahlte System (b) besonders unbeständig ist, wie aus der Tabelle 1 und Abb. 3 zu ersehen ist. Andere drei Präparate haben ungefähr ähnliche Beständigkeit. Nur das gekochte und dann USW.-bestrahlte System (d) zeigt wieder eine spezielle Eigenschaft und zwar dieses Präparat lässt nach dem Absetzen gröberer Teilchen die bläulich opaleszierende, typisch kolloidale Flüssigkeit hinter. Noch dazu ist dieses abgesetzte Präparat durch einfaches Handschütteln wieder zu milchweisses in Durchsicht orange-rotes System peptisierbar. Bei den anderen Proben findet solche Erscheinung auf keinem Fall statt, so dass das Sediment setzt nach wiederholten Schütteln sofort ab und die Flüssigkeit bleibt immer vollkommen klar. Die Tatsache, dass das USW.-bestrahlte Präparat (b) sehr unbeständig ist und wohingegen das gekochte und dann USW.-bestrahlte Präparat (d) ein typisches Kolloid-Verhalten vor sich zeigt, lässt uns erinnern, dass die USW. die entgegengesetzte, koagulierende und stabilisierende Wirkung ausgeübt hätten. Nach K. Söllner und C. Bondy[9] wirken die USW. auf System "flüssig/flüssig" emulgierend und auch koagulierend in gleicher Zeit. Da unser Fall von Schwefel-dispersem System nicht mit System "flüssig/flüssig" sondern mit "flüssig/fest" zu tun hat, kann man nicht gleicherweise behandeln. Obwohl das Experiment dafür noch ungenügend ist, möchte ich vorläufig folgendes hinweisen. Erstens, scheint die USW. im allgemeinen das Kristallwachstum zu beschleunigen. Die Unbeständigkeit des



(a) (b) (c) (d)

Abb. 3.

(8) *Angew. Chem.*, **49** (1936), 117.

(9) K. Söllner und C. Bondy, *Trans. Faraday Soc.*, **31** (1935), 835; **32** (1936), 616.

USW.-bestrahlten Präparats (b), würde dadurch hervorgerufen sein. Bei anderem Versuch habe ich auch gleiches Resultat erhalten.[10] Was dem letzten Fall betrifft, ist die Sache etwas anders. Es wurde hier das System erst erhitzt zum Sieden und dann mit USW. bestrahlt. Daraus möchte ich vermuten, dass es beim Kochen einige Schwefel-Verbindungen und ultramikroskopische Teilchen entstanden wäre. Diese Teilchen wurden durch nachfolgendes Bestrahlen von USW. im einzelnen zerteilt und die genannte Schwefel-Verbindungen wurden gleichzeitig an denen adsorbiert, die jetzt als Stabilisator die Beständigkeit des Systems verursacht hatten. Das ist also dieselbe Erscheinung, wie wir schon als USW.-Peptisation hingewiesen haben.[11] Die mikro- und ultramikroskopische Untersuchung erklärt das Verhalten sehr deutlich. Nämlich, in nur gekochtem Präparat (c) lassen auch viele ultramikroskopische Teilchen sich erkennen, die aber an der Oberfläche grösserer Kristallen kleben und kaum in Brownscher Bewegung sind; dahingegen in gekocht und dann USW.-bestrahltem Präparat (d) sind alle Teilchen in lebhafter Brownschen Bewegung sich befinden.

IV. **Über die Reaktion zwischen Schwefel und Quecksilber in dispersem Zustand.** E. Sauer[12] hat schon nachgewiesen, dass durch Reaktion von Schwefel und Quecksilber in kolloid-dispersem Zustand, das Quecksilbersulfid in schwarzer Modifikation sich entsteht. Zu diesem Zweck hat er die chemisch hergestellte sehr beständige Sole verwendet, in denen man annehmen muss, dass die Teilchen mit stabilisierendwirkenden Hüllen von Ionen bzw. Oberflächen-Verbindungen überzogen sind.[13] Wie erwähnt, konnte ich gerade das reine Schwefel-disperse System in hydrophobem Zustand erhalten. Da sich das Quecksilber durch einfaches Schütteln,[14] USW.-Bestrahlen[15] oder Dampf-Explosion[16] leicht dispergieren lässt, war es mir von Interesse die Reaktion beider Substanzen in hydrophob-dispersem Zustand nachzuprüfen.

Es wurde 5.0–7.5 c.c., wie oben erwähnt, hergestelltes Schwefel-disperses System und 0.5–1.0 c.c. reines Quecksilber in einem Probierglaschen zugeschmolzen. Diese Probe wurden mechanisch geschüttelt

(10) Nach noch unveröffentlichem Versuch von uns, wurde auch festgestellt, dass die Beständigkeit von Weimarnschem Schwefel-Sol auch durch Bestrahlen von USW. stark herabgesetzt wird.

(11) N. Sata und S. Watanabe, *Kolloid-Z.*, **73** (1935), 50; **78** (1937), 277; H. A. Wannow, *ibid.*, **81** (1937), 105.

(12) E. Sauer, *Kolloid-Z.*, **73** (1935), 45.

(13) N. Sata, dieses Bulletin, **11** (1936), 624; H. Freundlich, "Kapillarchemie", Bd. II, 191, Leipzig (1932).

(14) I. Nordlund, "Experimentelle Studien über Hg-Hydrosole", Dissertation, Upsala (1918); *Kolloid-Z.*, **26** (1920), 128; N. Sata, *ibid.*, **71** (1935), 48.

(15) *Kolloid-Z.*, **71** (1935), 48.

(16) Dieses Bulletin, **11** (1936), 443.

oder USW. bestrahlt, so dass dadurch dispergiertes Quecksilber sofort mit zusammenvorhandenem dispersen Schwefel reagieren würde. Weil der H_2S in diesem Fall die einzige Verunreinigung ist, wurden die Kontroll-Versuche mit H_2S-haltigen Systeme auch ausgeführt. Die Ergebnisse sind in folgender Tabelle 2 zusammengestellt.

Tabelle 2.

<table>
<tr><td rowspan="2">Zusammensetzung der Proben.</td><td colspan="2">H_2S-freie Systeme.</td><td colspan="4">H_2S-haltige Systeme.</td></tr>
<tr><td colspan="2">S-Sol (aus H_2S-Wasser hergestellt und H_2S ausgetrieben durch Kochen). Hg-Metall.</td><td>H_2S-Wasser. Hg-Metall.</td><td>H_2S-Wasser. S-Sol. Hg-Metall.</td><td>H_2S-Wasser. Hg-Metall.</td><td>H_2S-Wasser. S-Sol. Hg-Metall.</td></tr>
<tr><td>Anfängiger Befund.</td><td colspan="2">Milchweiss trübe mit orange-roter Durchsichtsfarbe.</td><td>Ganz klar.</td><td>Bläulichweiss getrübt mit Opaleszenz.</td><td>Ganz klar.</td><td>Bläulichweiss getrübt mit Opaleszenz.</td></tr>
<tr><td>Behandlung.</td><td>Maschine-Schütteln. (10 Min.)</td><td>USW. bestrahlt für 1 Min.</td><td colspan="2">Maschine-Schütteln. (10 Min.)</td><td colspan="2">USW. bestrahlt für 1 Min.</td></tr>
<tr><td>Gleich nach der Behandlung.</td><td colspan="2">Flüssigkeit ist grau undurchsichtig. Hg-Oberfläche ist schön goldgelb.</td><td colspan="2">Flüssigkeit ist bräunlich grau undurchsichtig. Hg-Oberfläche ist mit grauem Anflug bedeckt.</td><td colspan="2">Flüssigkeit ist grau undurchsichtig. Hg-Oberfläche ist schön goldgelb.</td></tr>
<tr><td rowspan="4"></td><td rowspan="2">Setzt nach 6–7 Tagen fast ganz klar ab.</td><td rowspan="2">Nach 6–7 Tagen ist es fast ganz klar und nur ein Spur bläulicher Opaleszenz ist erkennbar.</td><td colspan="4">Nach 1 Tag.</td></tr>
<tr><td>Braun undurchsichtig.</td><td>Gräulich braun undurchsichtig.</td><td>Gelblich braun undurchsichtig.</td><td>Gräulich braun undurchsichtig.</td></tr>
<tr><td colspan="2">Nach 1 Monat ist die Flüssigkeit ganz klar. Der Bodensatz ist schwarz u. durch Schütteln nicht wieder peptisierbar. Nach langem Stehen (5–6 Mon.) erleidet der Bodensatz gar keine Änderung.</td><td>Nach 7–8 Tagen setzt der undurchsichtige Teil ab. Die Flüssigkeit ist bläulich opaleszierend.</td><td>Nach 12 Tagen setzt wie nebenstehende ab.</td><td colspan="2">Nach 10 Tagen setzt der undurchsichtige Teil ab. Die Flüssigkeit zeigt Spuren von bräunlich weisser Trübung.</td></tr>
<tr><td colspan="2"></td><td colspan="4">Der Bodensatz ist anfangs gräulich braun. Seine Farbe ändert sich mit der Zeit zu rötlichem Ton u. nach 6–8 Mon. ist er schön zinnober-rot. Er ist durch Schütteln wieder peptisierbar u. bleibt etwa 1 Woche beständig.</td></tr>
</table>

Von der Ergebnissen der Tabelle 2, sollte folgendes hingewiesen werden.

(1) Wenn das System den H_2S in irgendwelcher Menge enthält, so entsteht gelb-oranges Sulfid und zwar in kolloid-dispersem Zustand. Nach C. Doelter[17] ergibt das Quecksilber und H_2S-Wasser bei der Wasserbad-Temperatur ein Gemisch von rotem und schwarzem Sulfid. Nach meinem Versuch wurde festgestellt, dass die ähnliche Reaktion bei Zimmertemperatur vor sich läuft, wenn das Quecksilber in dispersem Zustand vorhanden ist. Dass sich das entstandene gelbliche Sulfid seine Farbe mit der Zeit rötlicher ändert und nach 6–8 monatigem Stehen vollkommen zinnoberroten Farbton ergibt, stimmt einigermassen mit der Meinung von J. L. Proust.[17] Ausserdem ist es zu beachten, dass dieses Sulfid immer in fein-zerteiltem Zustand bleibt; d.h. ist das System nach dem Absetzen durch einfaches Schütteln wieder zu ziemlich beständigem System peptisierbar, welches 7–8 Tage beständig bleibt. Es bringt uns die Vermutung nahe, dass es ausser Sulfiden noch stabilisierend-wirkende Substanzen dabei entstanden wäre.

(2) Durch die Reaktion von reinem Quecksilber und Schwefel in hydrophob-dispersem Zustand, scheint nur das Sulfid in schwarzer Modifikation entstehen. Das Resultat ist also dasselbe wie bei der Reaktion in hydrophil-dispersem Zustand nach E. Sauer.[12] Dass die Hg-Oberfläche nach dem Schütteln goldene Farbe erhält, sollte der Beweis sein, dass der H_2S noch in Spuren geblieben war. Dann könnte er an der Hg-Oberfläche das goldgelbe Sulfid ausscheiden, wie bei obenerwähntem H_2S-haltigen System der der Fall war. Dieses schwarze Sulfid ist, nach dem Absetzen, im Gegenteil zu vorhergehendem Fall H_2S-haltiger Systeme, durch Schütteln nicht wieder beständig peptisierbar und der Niederschlag setzt sofort ab und die Flüssigkeit bleibt ganz klar. Da das System anfangs nach erstem Schütteln, etwa für eine Woche doch beständig bleibt, könnte man schliessen, dass die Teilchen in diesem Fall mit der Zeit von amorph-kolloidal zu grob-kristallin sich verändert hätten. Die kristallographische Zustandsänderung der Niederschlägen durch Altern ist schon eine wohlbekannte Tatsache.[18]

(3) Das gemeinsame Vorhandensein von H_2S und disperses Schwefel scheint nur den additive Einfluss ausüben und zwar erhält das System gräulich braune Trübung, von denen der gräuliche Ton ziemlich schnell verschwindet.

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(17) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Bd. IV, 946, London (1923).

(18) *Kolloid-Z.*, **73** (1935), 55.

(4) Von der Menge des entstandenen Niederschlags erkennt man sich darauf, dass die Wirkung von USW. hier viel schwächer ist, als die des mechanischen Schüttelns. Ausserdem ist es besonders zu bemerken, dass das Reaktionsprodukt durch USW.-Bestrahlen und mechanisches Schütteln qualitativ ganz gleichartig ist. Daraus könnte man konstatieren, dass die USW. in diesem Fall keine eigenartige Wirkung vor sich gezeigt hatten, wie bei einige anderen Fällen.[19]

Zusammenfassung.

(1) Eine neue einfache Methode der Herstellung hydrophob-disperses Systems von Schwefel ist beschrieben.

(2) Die Methode besteht darin, dass man das H_2S-Wasser unter bestimmten Bedingung durch Hitze zersetzt und das Schwefel in kolloiddispersem Zustand ausscheiden lässt.

(3) Wenn man übrich bleibenden H_2S durch verschiedenen Behandlungen (Kochen, Bestrahlen von USW. oder die beide) austreibt, so zeigen die Systeme auch verschiedenen Absetzungsvorgänge, je nach der Behandlungsart.

(4) Die mikro- und ultramikroskopische Untersuchung an den Bodensatz hat gezeigt, dass die USW. eine interessante Wirkung auf der Keimbildung und dem Kristallwachstum ausüben.

(5) Die chemische Reaktion von hydrophob-dispersem Schwefel und Quecksilber unter Wirkung von Maschine-Schütteln bzw. USW.-Bestrahlen wurde untersucht.

(6) Es wurde dadurch festgestellt, dass wenn das System den H_2S als Verunreinigung enthält, das gelbe bis orange Sulfid entstehen wird und nur das schwarze Sulfid, wenn kein H_2S vorhanden ist.

(7) Vor der Natur und der Menge der Reaktionsprodukte wurde konstatiert, dass hier die Wirksamkeit von USW. und Maschine-Schütteln qualitativ ganz gleich, nur aber quantitativ verschieden ist.

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(19) *Kolloid-Z.*, **73** (1935), 50; **78** (1937), 277.

Optical Rotatory Power of *l*-Menthol in Heavy Methyl Alcohol.

By Eijiro OGAWA.

(Received November 15th, 1937.)

The author[1] measured specific rotatory power of *d*-tartaric acid in ordinary water and 2.15% heavy water and obtained the results given in Table 1.

Table 1.

Solvent	$[\alpha]_D^{29.0}$	$[\alpha]_D^{26.9}$
2.15% Heavy water	8.84°	8.56°
Ordinary water	8.89°	8.60°

This difference was explained quantitatively by the decrease of hydrogen ion concentration under the assumption that the degree of dissociation of *d*-tartaric acid in heavy water is the same as acetic acid.

Biilmann, Jensen, and Knuth[2] observed the specific rotatory power $[\alpha]_D^{20} = +0.40°$ in 2-deutero-camphane.

The present author[3] carried out the following experiments: 2.5 g. of *l*-menthol was dissolved in 7 c.c. of ordinary methyl alcohol or 27.5% heavy methyl alcohol. No difference in specific rotatory power was observed (Table 2).

Table 2.

Solvent	α	$[\alpha]_D^{14.4}$
Ordinary methyl alcohol	17.49°	48.63°±0.03°
27.5% Heavy methyl alcohol	17.49°	48.63°±0.03°

(1) *Tech. Repts. Kyushu Imp. Univ.*, **11** (1936), 21.
(2) *Ber.*, **69** (1936), 1031.
(3) *Tech. Repts. Kyushu Imp. Univ.*, **12** (1937), 169.

From these results it is concluded that the difference of specific rotatory power in pure heavy methyl alcohol is at most 0.10° and the isotopic effect in hydroxyl bond has little influence upon the field of asymmetric carbon atom.

Recently H. Erlenmeyer and H. Schenkel[4] observed remarkable differences in specific rotatory power in *l*-mandelic acid and *d*-atrolactic acid namely 5.83° ± 0.26° and 1.19° ± 0.2° respectively. In these cases the isotopic effect upon the field around asymmetric carbon atom are remarkable as compared with camphane or menthol. This is probably due to cyclic nature of latter molecules.

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(4) *Helv. Chim. Acta*, **19** (1936), 1199, 1381.

AUTHOR INDEX TO VOLUME 12, 1937.

ABÉ, Mochiyuki. See UÉMURA, Taku.

ADZUMI, Hiroshi. Studies on the flow of gaseous mixtures through capillaries. I. The viscosity of binary gaseous mixtures 199

Studies on the flow of gaseous mixtures through capillaries. II. The molecular flow of gaseous mixtures 285

Studies on the flow of gaseous mixtures through capillaries. III. The flow of gaseous mixtures at medium pressures 292

On the flow of gases through a porous wall 304

AKABORI, Shiro, and OKAHARA, Kunio. Über die chemische Natur der Taka-Amylase. I. Enzymatische Verdauung von Taka-Amylase-Präparaten durch Proteinasen 55

AKABORI, Shiro. See also TOI, Bun-ichi.

AKIYAMA, Hajime. See TAMAMUSHI, Bunichi.

ANDO, Toshio. See URUSHIBARA, Yoshiyuki.

AOYAMA, Shin-ichi, and KANDA, Eizo. Studies on fluorine at low temperatures. I. Preparation, analysis and handling of fluorine 409

Studies on fluorine at low temperatures. II. Vapour pressure of fluorine 416

Studies on Fluorine at low temperatures. III. Dissolution of chlorine in liquid fluorine 455

Studies on fluorine at low temperatures. IX. Experiment on the reaction between solid fluorine and liquid hydrogen 521

ARAKI, Hisakazu. See URUSHIBARA, Yoshiyuki.

ARIYAMA, Kyozo. A theory of surface tension of Debye-Hückel electrolyte 32

A theory of surface tension of ternary solutions 38

A note on the osmotic coefficient and the activity coefficient at the surface 44

A theory of surface tension of aqueous solutions of inorganic acids .. 109

A note on the theory of surface tension of ternary solutions 114

Note on a theory of the expanded film 335

DEHN, William M. See PEARL, Irwin A.

FUKUNAGA, Shozo. See IWADARE, Koichi.

HAN, Kwan. See MATSUNO, Kichimatsu.

HARADA, Takeshi. See TAKAYAMA, Yoshitaro.

HIGASI, Ken-iti, and KUBO, Masaji. The dielectric constant of cetyl alcohol near its melting point 326

ICHIKAWA, Nobutoshi. Studies on the constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. II. On the reduction and bromination of shonanic acid 233

Studies on the constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. III. Studies on the oxidation of shonanic acid 243

Studies on the constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. IV. On dihydroshonanyl alcohol and the optical activity of shonanic acid and its derivatives 253

Studies on the constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. V. Studies on the oxidation of dihydroshonanyl alcohol and the ozonolysis of shonanic acid 258

Studies on the constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. VI. Studies on the oxidation of dihydroshonanic acid with ozone and potassium permanganate 267

INOUE, Yoshiki. See MIZUSHIMA, San-ichiro.

ISHIKAWA, Tetsuya. The viscosity of mixed salt solution 16

IWADARE, Koichi, FUKUNAGA, Shozo, and KUBOTA, Bennosuke. The formation of *l*-threose 116

JOSHI, Shridhar Sarvottam, and KULKARNI, Sadashiv S. "Zonal effect" in the slow coagulation of colloid arsenious sulphide 145

KANDA, Eizo. Studies on fluorine at low temperatures. IV. Separation of fluorine from oxygen by adsorption and rectification 458

Studies on fluorine at low temperatures. V. Viscosity of fluorine gas at low temperatures 463

Studies on fluorine at low temperatures. VI. Surface tension of liquid fluorine 469

Studies on fluorine at low temperatures. VII. Determination of dielectric constants of condensed gases 473

Studies on fluorine at low temperatures. VIII. Determination of molecular heat, heat of fusion of condensed fluorine and the entropy of fluorine 511

See also AOYAMA, Shin-ichi.

KASHIMOTO, Shin, and KOBAYASHI, Masahisa. The third absorption bands of co-ordination compounds. IV. [Co *dg*$_2$′ *py* Cl], [Co$(NH_3)_2(NO_2)_2ox]NH_4 \cdot H_2O$ and [Co $ox_3]K_3 \cdot 3.5H_2O$ 350

KIMURA, Osamu. Études de l'effet du champ électrique sur la viscosité des liquides. I 147

KINOSHITA, Kyôji. On the end-point voltage of the lead-acid storage cell 25

On the silver oxide positive of the alkaline accumulator. I 164

On the silver oxide positive of the alkaline accumulator. II 366

KOBAYASHI, Masahisa. See KASHIMOTO, Shin; TSUCHIDA, Ryutaro.

KOIZUMI, Masao, and TITANI, Toshizo. Austausch der Wasserstoffatome zwischen Pyrrol und Wasser. (Vorläufige Mitteilung.) 107
KOMORI, Saburo, and UENO, Sei-ichi. On a new unsaturated fatty acid, $C_{16}H_{18}O_2$, present in the oil of *Rindera obtusiloda* 226
Studies on the unsaturated lower fatty acids. On the crystalline derivatives of the unsaturated lower fatty acids 433
KONYA, Hideo. See MATSUDA, Ryoichi.
KUBO, Masaji. See HIGASI, Ken-iti.
KUBOTA, Bennosuke. See IWADARE, Koichi.
KULKARNI, Sadashiv S. See JOSHI, Shridhar Sarvottam.

MAEDA, Shigeo. Über die chemische Natur des Papains 319
MASAKI, Kôiti. The absorption spectra of nitrocellulose 1
MATSUBARA, Tamaki. Über die Konstitution des Cerberins 436
MATSUDA, Ryoichi, KONYA, Hideo, and NISHIMORI, Teruichi. The electrolytic formation of persulphate. Part IV. Influence of temperature 425
MATSUDA, Ryoichi, and NISHIMORI, Teruichi. The electrolytic formation of persulphate. Part III. Study of the electrodes 331
MATSUNO, Kichimatsu, and HAN, Kwan. Studies on the Raman effect of organic substances. VIII. Raman effect of furane derivatives 155
MIDUNO, Saburo. See TAKAYAMA, Yoshitaro.
MIYAKE, Moriji. See SAMESHIMA, Jitsusaburo.
MIYAMOTO, Susumu. Chemical reactions in the silent electric discharge. XVI. Reactions between hydrogen and solid inorganic compounds 313
MIZUSHIMA, San-ichiro, MORINO, Yonezo, and INOUE, Yoshiki. A note on the polymerisation of styrene as revealed by the Raman effect 136
MIZUSHIMA, San-ichiro, UEHARA, Yasuo, and MORINO, Yonezo. The OH-vibration spectrum in the photographic infrared 132
MORINO, Yonezo. See MIZUSHIMA, San-ichiro.
MORITA, Noriyoshi, and TITANI, Toshizo. Der katalytische Isotopenaustausch zwischen Wasser und Sauerstoff 104

NAKAMURA, Morizumi. See UHARA, Ituro.
NISHIMORI, Teruichi. See MATSUDA, Ryoichi.
NIWASE, Yosiaki. See SATA, Naoyasu.

ÔEDA, Haruomi. Catalytic hydrogenation of amides of α-hydroxy-acids 121
Catalytic hydrogenation of amides of -hydroxy-acids (Continued) 377
OGAWA, Eijiro. Optical rotatory power of *l*-menthol in heavy methyl alcohol 545
OKABE, Kenzo, and TITANI, Toshizo. Über den Gehalt der atmosphärischen Feuchtigkeit an schwerem Wasser 11
OKAHARA, Kunio. See AKABORI, Shiro.
OKAMOTO, Go. See TOMINAGA, Hitoshi.
OOSAKA, Hazime. Cryoscopic studies on the transition points of the compounds of organic solvents with salts. III. The congruent melting points of some alcoholates of alkali halides 177
OZAWA, Asaitirô. See URUSHIBARA, Yoshiyuki.

PEARL, Irwin A., and DEHN, William M. An isomer of cymene from camphor .. 493

SAKURAI, Buhei. Electrolytic reduction of maleimide and pyrroline 8
SAMESHIMA, Jitsusaburo, and MIYAKE, Moriji. Studies on the oiliness of liquids. III. Measurements of the kinetic friction coefficients 96
SAMESHIMA, Jitsusaburo, and TSUBUKU, Yasuji. Studies on the oiliness of liquids. IV. Measurements of the static friction coefficients by the method of inclination 127
SATA, Naoyasu. Über das durch Zersetzen von Schwefelwasserstoffwasser hergestellte disperse System von Schwefel und dessen Reaktion mit dispersem Quecksilber 536
SATA, Naoyasu, and NIWASE, Yosiaki. Die kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten. II. System Benzol-Wasser-Methylalkohol und Tetrachlorkohlenstoff-Wasser-Methylalkohol 86
SHISHIDO, Hideo. Synthese des Domesticin-äthyläthers 150
Synthese von einem Isomeren des Domesticin-äthyläthers 419
SIMAMURA, Osamu. See URUSHIBARA, Yoshiyuki.
SUEDA, Hideo. Recherches sur la concentration des ions d'hydrogène contenus dans les solutions aqueuses des ammines-cobaltiques complexes et sur leurs spectres d'absorption. III. Solutions aqueuses des complexes renfermant le radical nitro 71
On the relation between the configuration of metallic complex salts and their absorption spectra 188
Studies on the aqueous solutions of some chromic salts. I. Spectrochemical studies of the chloro-aquo compounds 480
Studies on the aqueous solutions of some chromic salts. II. Modified green chromic sulphate, ol green chromic chloride and green chromic sulphate 524
SUÉDA, Hidéo. See SUEDA, Hideo.

TAKANO, Masakichi. Studies on the partial hydrogenation of fish oil. VIII. The constituents of docosatrienic acid produced on hydrogenating methyl clupanodonate 395
TAKASE, Shin-ichiro. See UENO, Sei-ichi.
TAKAYAMA, Yoshitaro, HARADA, Takeshi, and MIDUNO, Saburo. Studies on amino-acids and related compounds. Part XI. The formation of aldehydes by the electrolytic oxidation of α-amino-acids 342
TAKAYAMA, Yoshitaro, and MIDUNO, Saburo. Studies on amino-acids and related compounds. Part X. Electrolytic oxidation of aspartic acid and malonic acid 338
TAKEBAYASHI, Matsuji. See URUSHIBARA, Yoshiyuki.
TAMAMUSHI, Bunichi, and AKIYAMA, Hajime. The paramagnetic isomerisation of maleic acid into fumaric acid in aqueous solution 382
TITANI, Toshizo. See KOIZUMI, Masao; MORITA, Noriyoshi; OKABE, Kenzo.
TOI, Bun-ichi, and AKABORI, Shiro. Ein neues Verfahren zur Synthese von Pyrrol-Derivaten 316

TOMINAGA, Hitoshi, and OKAMOTO, Go. Spektroskopische Studien über Reaktionsflammen. I. Die Reaktionsflamme von Acetylen und Halogen 401

Spektroskopische Studien über Reaktionsflammen. II. Die Reaktionsflamme von Quecksilber und Halogen 404

TSUBUKU, Yasuji. See SAMESHIMA, Jitsusaburo.

TSUCHIDA, Ryutaro. Measurement of circular dichroism in the ultra-violet regions. I. 276

TSUCHIDA, Ryutaro, and KOBAYASHI, Masahisa. The third absorption bands of co-ordination compounds. III. The configuration of [Co dg_2' NH_3 Cl]. A new type of optically active complex radicals 83

TSUZUKI, Yojiro. Condensation of diethyl tartrate with cyclic ketones and the molecular rotation of the resulting compounds 487

UEHARA, Yasuo. See MIZUSHIMA, San-ichiro.

UÉMURA, Taku, and ABÉ, Mochiyuki. Études spectrochimiques des matières colorantes dérivées de la quinone-imine 59

UENO, Sei-ichi, and TAKASE, Shin-ichiro. Über eine hochungesättigte Fettsäure $C_{24}H_{38}O_2$ aus dem Öle des Thunfisches, *Tynnus tynnus* L 453

UENO, Sei-ichi. See also KOMORI, Saburo.

UHARA, Ituro, and NAKAMURA, Morizumi. Adsorption of solvent vapour by the solute crystal 227

UMEZAWA, Sumio. Synthetische Versuche in der Selenophen-Gruppe. III. β-Nitroselenophen und die Orientierung im Selenophen-Kern 4

URUSHIBARA, Yoshiyuki, and ANDO, Toshio. The photochemical dehydrogenation of 7-dehydrocholesterol and the pyrolysis of the product 495

URUSHIBARA, Yoshiyuki, ANDO, Toshio, ARAKI, Hisakazu, and OZAWA, Asaitirô. Some cholesterol derivatives 353

URUSHIBARA, Yoshiyuki, and SIMAMURA, Osamu. The effect of oxygen and reduced nickel on the catalytic action of hydrogen bromide in the isomerization of isostilbene into stilbene 507

URUSHIBARA, Yoshiyuki, and TAKEBAYASHI, Matsuji. The addition of hydrogen bromide to allyl bromide in the presence of various substances. IV. The effect of the ferro-magnetic metals free from oxides. Remarks on the catalytic action of the ferro-magnetic metals and oxygen 51

The addition of hydrogen bromide to allyl bromide in the presence of various substances. V. A comparison of the effect of oxygen with that of peroxide. The relation between the amount of oxygen present and the result of addition 138

The addition of hydrogen bromide to allyl bromide in the presence of various substances. VI. The homogeneity of the catalytic action of oxygen. A theory of the oxygen effect 173

A note on the Cannizzaro reaction 328

The effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride 356

The effects of oxygen and peroxides on the rate of addition of bromine to cinnamic acid in carbon tetrachloride 499

YAMASAKI, Kazuo. Absorptionsspektren von Metallkomplexsalzen des 2,2'-Dipyridyls. I 390
YOSHIMURA, Hisato. Effect of water on the potential of the glass electrode 359
Studies on the nature of the glass electrode potential. III. On the cause of the asymmetry potential of the glass electrode 443

CORRECTIONS TO VOLUME 12, 1937.

Page	Line	
22	6	*for* "$\eta^{(1-z_v)+kz_v} = \eta_1^{(1-z_v)} + \eta_2^{kz_v}$" *read* "$\eta^{(1-z_v)+kz_v} = \eta_1^{(1-z_v)} \cdot \eta_2^{kz_v}$"
23	Table 7	*for* "Formula (13)" *read* "Formula (14)"
"	"	*for* "Formula (14)" *read* "Formula (13)"
24	Table 8	*for* "Formula (13)" *read* "Formula (14)"
"	"	*for* "Formula (14)" *read* "Formula (13)"
119	6	*for* "tetracetyl lead" *read* "lead tetracetate"
389	8	*for* "accerelated" *read* "accelerated"
434	Legend to Fig. 1.	*for* "Tempertuare" *read* "Temperature"